STANFORD-USGS SHRIMP-RG ION MICROPROBE: A NEW APPROACH TO DETERMINING THE DISTRIBUTION OF TRACE ELEMENTS IN COAL

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ABSTRACT

The distribution of Cr and other trace metals of environmental interest in a range of widely used U.S. coals was investigated using the Stanford-USGS SHRIMP-RG ion microprobe. Using the oxygen ion source, concentrations of Cr (11 to 176 ppm), V (23 to 248 ppm), Mn (2 to 149 ppm), Ni (2 to 30 ppm), and 13 other elements were determined in illite/smectite, a group of clay minerals commonly present in coal. The results confirm previous indirect or semi-quantitative determinations indicating illite/smectite to be an important host of these metals. Calibration was achieved using doped aluminosilicate-glass synthetic standards and glasses prepared from USGS rock standards. Grains for analysis were identified optically, and confirmed by 1) precursory electron microprobe analysis and wavelength-dispersive compositional mapping, and 2) SHRIMP-RG major element data obtained concurrently with trace element results. Follow-up investigations will focus on the distribution of As and other elements that are more effectively ionized with the cesium primary beam currently being tested.

INTRODUCTION

Research on the occurrence of potentially toxic trace metals in coal is fundamental to predicting the potential for distribution of these metals to the environment through coal combustion, mining, and leaching from storage piles. Microbeam instruments with good spatial resolution and element sensitivities are needed to make direct, in-situ trace-element determinations that are specific to individual coal components. The Sensitive High-Resolution Ion Microprobe with Reversed Geometry (SHRIMP-RG) at Stanford University offers these characteristics. The reversed geometry, in which the electrostatic sector is downstream of the magnetic sector of the mass spectrometer, gives the SHRIMP-RG superior mass-resolution compared to its forward geometry (FG) SHRIMP predecessor and smaller ion probes.

Our initial use of the SHRIMP-RG for coal samples focussed on the distribution of Cr and other transition metals in illite/smectite, a common inorganic clay mineral constituent of coal and other sediments. Previous work, including studies by selective leaching, electron microprobe, and XAFS spectroscopy (Huggins et al., 2000) and chemical analysis of mineral separates (Palmer and Lyons, 1996), indicates a significant residence for Cr in clay minerals in coal. This study was undertaken to confirm and quantify these results, and to demonstrate the utility of the SHRIMP-RG for studies in environmental geochemistry. Understanding the mode of occurrence of Cr in coal is especially important because the hexavalent form of the element is a known carcinogen.

SAMPLE CHARACTERIZATION AND ANALYSIS METHODS

Samples studied include three coals currently being investigated by the USGS in Phase II of a larger DOE-funded study of toxic substances from coal combustion. The three Phase II coals are a bituminous Ohio 5/6/7 blend, a sub-bituminous Wyodak sample, and a North Dakota lignite. Three additional samples were investigated, a bituminous Illinois #6 sample from Phase I of the combustion study, a Northern Appalachian (Pittsburgh) bituminous sample and a second Illinois #6 sample studied by the USGS as part of another recent contract. Each of these samples has been very well characterized by conventional coal-testing methods, bulk geochemistry, mineralogy, and element modes of occurrence, including selective leaching, electron microprobe, and for all but the Pittsburgh and second Illinois #6 samples, bulk XAFS analysis.

Preliminary work involved characterization of illite/smectites using a JEOL 8900R electron microprobe for quantitative analysis and wavelength-dispersive elemental mapping. SHRIMP-RG data were obtained in August, 1999 and February, 2000, using an O_2^- duoplasmatron source. Analysis points were initially subjected to a 1-3 minute burn-in to stabilize the response. The burn-in was followed by a "short" analysis consisting of 4, 7, or 8 elements, to confirm the identity of the grains selected and minimize the contribution of overlapping grains. In the August, 1999 runs, the short analyses were followed directly by "long" analyses in which the initial 7 elements (Mg, Al, Ca, Si, ^{52}Cr, K, and Fe) were re-determined and combined with analyses of Sc, Ti, V, ^{53}Cr, Mn, Co, Ni, Cu, Zn, Rb, and Sr. The same procedure was used to measure these elements in reference standards. A similar procedure was followed in February, 2000, except that all the short runs were conducted successively, followed by a series of long runs for only the most promising grains. This modification minimized magnet instability caused by changes to its within-run scan range. Quantifying the concentration of Cr was the highest priority of the study, and therefore, Cr was determined twice, as ^{52}Cr and as ^{53}Cr. Using this approach, the natural ratio of $^{53}Cr/^{52}Cr$ (0.1134) was typically reproduced to three decimal places. Concentrations obtained using the two chromium isotopes were generally within 1% (absolute), for calibrations obtained using the same standard (Table 1).

A variety of aluminosilicate standard glasses were investigated, including National Institute of Standards and Technology (NIST) SRM glasses 610 and 612, glass synthetic standards GSE and GSD, prepared for the USGS by Corning Glass Works, Inc., and glass prepared from powdered USGS rock standard BHVO-1. Concentrations were obtained by determining the counts/ppm for standards and calculating the concentrations of unknowns by comparing their raw counts to the standard data. Calibration results obtained using three different standards, SRM 610, GSE, and BHVO-1, for the same Ohio 5/6/7 illite/smectite, are given in Table 1. From electron microprobe analysis, the SiO_2 and Al_2O_3 contents of illite/smectite are known to be about 50 and 30 weight percent, respectively. SHRIMP-RG results for these elements are given in weight percent to facilitate comparison to the microprobe data (Table 1). For most elements, the GSE standard gives the lowest concentrations, and these can be considered minima (Table 1). GSE is the only standard determined in every SHRIMP-RG run, providing a uniform basis for comparing data from each of the runs and for all of the samples. Table 2 shows the reproducibility of counts/concentration for the GSE standard in 4 runs over a 2-day period in February, 2000. Total deviation ranges from 5.8 to 12.5%, except for Rb (20.9%) and Sr (17.9%).

Table 1. SHRIMP-RG Data Reduction and Comparison of Standards for an Ohio 5/6/7 Illite/Smectite.

August 1999	*Raw Counts*	Counts/ppm (Al_2O_3, SiO_2 in wt. %)			Concentration (ppm) (Al_2O_3, SiO_2 in wt. %)		
Ohio 5/6/7		*SRM 610*	*GSE*	*BHVO*	*Conc. 610*	*Conc. GSE*	*Conc. BHVO*
Mg	*21391*	*9.44*	*13.00*	*13.06*	*2266*	*1645*	*1637*
Al_2O_3	*325487*	*10252*	*16810*	*11708*	*31.75*	*19.36*	*27.80*
Ca	*5442*	*12.68*	*15.57*	*14.59*	*429.2*	*349.5*	*373.0*
SiO_2	*1059325*	*18292*	*27723*	*19627*	*57.91*	*38.21*	*53.97*
Sc	*4163*	*362.6*	*240.5*	*349.6*	*11.48*	*17.31*	*11.91*
Ti	*29024*	*18.13*	*20.55*	*17.24*	*1601*	*1413*	*1683*
V	*13766*	*175.0*	*190.0*	*129.8*	*78.68*	*72.47*	*106.04*
^{52}Cr	*14022*	*180.2*	*215.9*	*163.0*	*77.82*	*64.95*	*86.01*
^{53}Cr	*1587*	*20.25*	*24.53*	*18.53*	*78.37*	*64.72*	*85.65*
Mn	*7009*	*200.6*	*303.2*	*253.2*	*34.94*	*23.12*	*27.69*
Co	*173*	*108.3*	*186.0*	*165.0*	*1.60*	*0.93*	*1.05*
Ni	*687*	*21.94*	*43.81*	*34.70*	*31.30*	*15.67*	*19.79*
Rb	*68370*	*617.4*	*718.8*	*584.2*	*110.74*	*95.12*	*117.02*
Sr	*11821*	*239.3*	*280.4*	*233.1*	*49.40*	*42.15*	*50.70*

Table 2. SHRIMP-RG Results- Reproducibility of the GSE Standard.

	GSE standard counts per ppm (Al_2O_3, SiO_2 in counts/wt. %)				
Date	2 Feb 00	2 Feb 00	3 Feb 00	3 Feb 00	% Total
Run #	1	2	3	4	Deviation
^{26}Mg	236.5	227.5	230.0	222.7	5.8
^{43}AlO	48462	46832	50470	47871	7.2
^{44}Ca	44.88	43.00	46.70	44.14	7.9
^{44}SiO	81609	79336	85734	81213	7.4
^{45}Sc	762.3	738.3	798.6	728.8	8.7
^{47}Ti	63.08	60.09	66.63	61.58	9.8
^{51}V	608.0	572.0	644.1	585.8	11.0
^{52}Cr	650.5	611.0	664.6	618.6	8.6
^{53}Cr	72.98	68.83	75.45	69.67	8.8
^{55}Mn	864.3	844.1	897.6	827.7	7.8
^{55}KO	7.17	6.97	7.30	6.71	6.8
^{59}Co	475.9	474.3	493.0	446.3	9.5
^{60}Ni	103.8	104.1	107.07	96.12	11.0
^{63}Cu	165.3	166.7	170.9	151.2	11.5
^{64}Zn	84.54	87.33	85.92	76.38	12.5
^{72}FeO	15.82	15.67	16.33	14.67	10.2
^{85}Rb	1673.3	1673.4	1926.4	1523.8	20.9
^{88}Sr	736.0	723.9	866.0	710.6	17.9

SHRIMP-RG RESULTS FOR ILLITE/SMECTITE

Chromium concentrations in illite/smectite in these coals range from 11 to 176 ppm (Fig. 1a). The results are consistent with semi-quantitative estimates obtained from previous electron microprobe data, leaching results, and XAFS (Huggins et al., 2000). Results for the Ohio and Pittsburgh samples are co-linear for Cr and V, possibly indicating a similar diagenetic history for these illites from the northern Appalachian Basin. Concentration ranges for some other elements of environmental interest in illite/smectite are as follows: V (23 to 248 ppm); Mn (2 to 149 ppm); and Ni (2 to 30 ppm; Fig. 1b-d). Trace element contents generally increase with the Mg content of the illite/smectite.

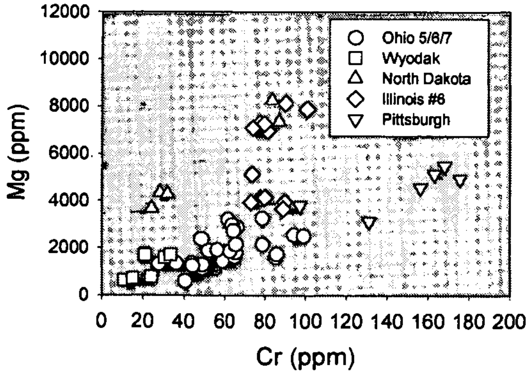
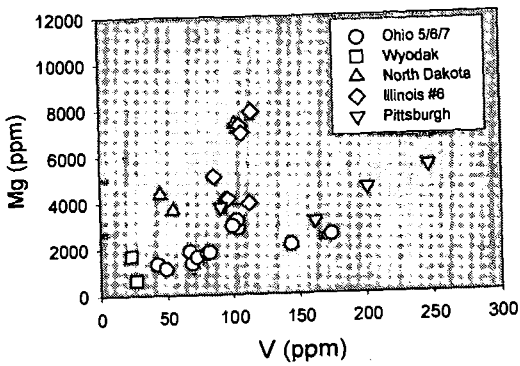
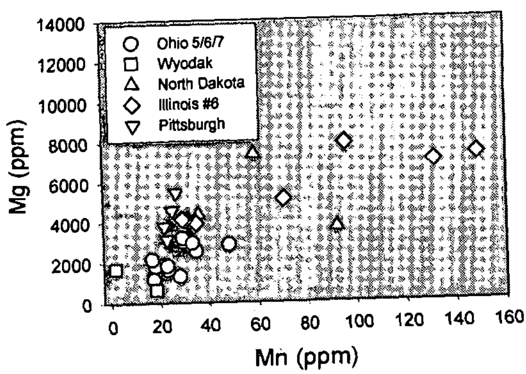


Figure 1a). Plot of Mg vs. Cr in illite/smectite from six coal samples, based on single-standard calibration using results for GSE. Illinois #6 data are for different two samples.





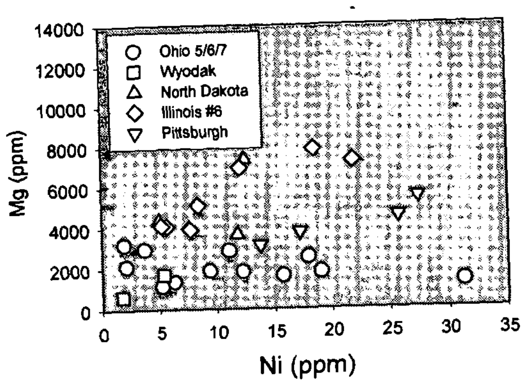


Figure 1b-d). Plots of V, Mn, and Ni vs. Mg in illite/smectite from six coal samples, based on calibration using GSE standard. Illinois #6 data are for two different samples.

PLANNED INVESTIGATIONS

The results reported here were determined using the SHRIMP-RG in its current configuration, in which oxygen (O_2^-) ions form the primary beam. Work is now being planned to take advantage of a high-energy Cs^+ ion source that is expected to be available for use in the summer of 2000. In the first planned study, the distribution of arsenic in fly ash particles will be investigated with the SHRIMP-RG. This study is prompted by evidence that moderately to slightly volatile elements such as Se and As, condense on the surface of fly ash particles as they cool, contributing to the health risk from inhaled particles and the leachability of toxic elements into the environment (EPRI, 1998). Using the oxygen source, we conducted a number of preliminary tests on fly ash from a Kentucky power plant, and on the aluminosilicate glass standards. These tests showed that the ^{75}As peak could be resolved from potential interferences in the GSE standard, whereas a mass scan on fly-ash in which ^{75}As was present also showed a larger and broader unknown peak that is not completely resolvable from the analytical peak using oxygen ions. Count rates for arsenic are expected to be an order of magnitude higher with the cesium source.

SUMMARY

This paper reports our initial use of the SHRIMP-RG ion microprobe for determining trace metal contents in illite/smectite, a common mineral constituent of coal and sediments. Results confirm and quantify the concentration of Cr in illite/smectite inferred from previous indirect or semi-quantitative studies. This knowledge is important in developing quantitative models for the behavior of Cr during coal processing and combustion. Planned SHRIMP-RG investigations will use a Cs^+ ion beam to more effectively ionize metals such as As and Hg, thereby improving their detection and analysis.

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